

Proton Magnetic Resonance Spectra of Acetylenic Fatty Acids

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The proton magnetic resonance spectra (PMR) of carbon tetrachloride solutions of C_{18} fatty acids were studied. The types of compounds include those in which the methylene chain is interrupted by one or two carbon-carbon triple bonds. Such bonds in long-chain acids tend to cause the appearance of anomalous lines in the PMR spectra. These lines are not expected *a priori*, especially because they do not appear in the spectra of the unsaturated fatty acids. No assignment of these lines has been made. The spectra presented are discussed from two points of view: the spectral effects produced by the triple bonds, and the possibility of using the line positions and multiplet structure of the anomalous lines to determine the position of a triple bond in a long-chain molecule.

IN OUR STUDY of the proton magnetic resonance spectra of long-chain carboxylic acids, we have previously considered the spectra of unsaturated C_{18} fatty acids (1). Among those acids were *trans*-octadec-11-en-9-ynoic acid and 10,12-octadecadiynoic acid. The spectrum of the former exhibits two anomalous lines, as yet unassigned, in the vicinity of $\delta = 1.3$ ppm. No such lines were observed in the spectra of the latter or of the other unsaturated acids. Apparently the anomalous lines are due to the presence of the carbon-carbon triple bond.

The present communication describes the high resolution 60-MHz PMR spectra of a series of acetylenic C_{18} fatty acids, noting in particular the presence or absence of any anomalous lines. The series includes straight-chain C_{18} acids with one carbon-carbon triple bond in various locations along the methylene chain, the methyl esters of two of the acids, and one acid with two conjugated triple bonds. The highly complex spin systems of the protons in long-chain molecules often give rise to broad, unresolved or partially resolved multiplets, which are the result of a large number of closely spaced transitions. A detailed analysis of the resulting spectra is not always possible. Nevertheless, observed spectra are useful for chemical structure determinations.

EXPERIMENTAL

The 60-MHz spectra of all samples were obtained at ambient temperature—i.e., $33^\circ \pm 1^\circ$ C in the magnet air gap—with a Varian DA-60IL spectrometer. Tetramethylsilane (Anderson Chemical Co., Weston, Mich.) was used as an internal reference. Each frequency-sweep spectrum was recorded four times on precalibrated chart paper with alternate upfield and downfield sweeps. The sweep rate was 0.5 Hz/second. Line position values are based on the averages of the measured line positions. The delta scale is used to report multiplet positions, where $\delta = 0.00$ for tetramethylsilane with positive values to low field. The positions of the various multiplets, given in Table I, are located by stating the position of the midpoint.

Pure crystalline or liquid samples were dissolved in carbon tetrachloride (Spectroquality Reagent, Matheson, Coleman and Bell, East Rutherford, N. J.) which was used without further purification. The concentration range of the solu-

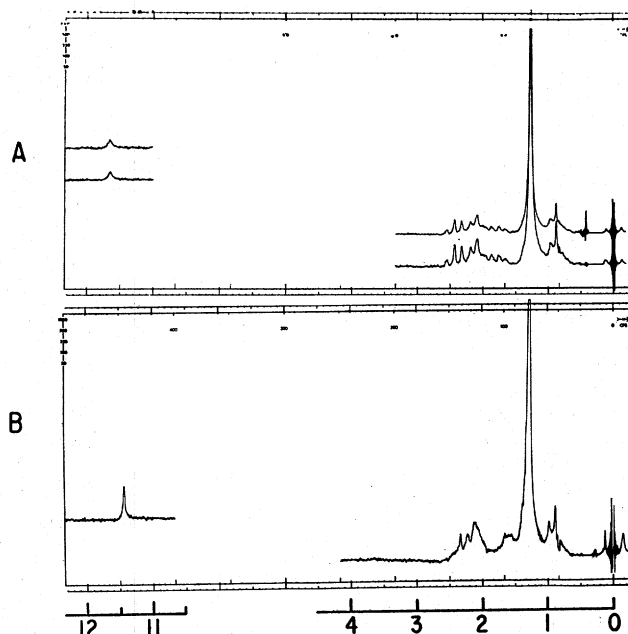


Figure 1. A. 5-Octadecynoic acid. B. 6-Octadecynoic acid

tions was 0.3 to 0.4M. The various pure octadecynoic acids were obtained from the Morton Chemical Co., Chicago, Ill. The methyl esters of 7- and 8-octadecynoic acids were prepared according to the procedure of Luddy, Barford, and Riemenschneider (2). The purity was confirmed by GLC. *trans*-Octadec-11-en-9-ynoic acid (santalbic acid), m.p. 38.5° – 39.5° C, was obtained from santalum album seed oil by the procedure of Gunstone and Russell (3).

RESULTS AND DISCUSSION

The structural formulas of the investigated compounds and the observed multiplet positions are listed in Table I. The PMR spectra of saturated long-chain carboxylic acids, which could be regarded as the parent compounds of the acetylenic derivatives, exhibit three main multiplets (1, 4, 5). A high-field triplet at $\delta = 0.87$ to 0.92 corresponds with the terminal methyl group. The chain methylene groups produce a broad band at $\delta = 1.25$ to 1.35 . A low-field triplet at $\delta = 2.25$ to 2.35 is produced by the α -methylene group, adjacent to the carboxyl group. For a given acid at room temperature the complexity of the spin system causes the triplet of the terminal methyl group to be somewhat broadened and distorted. Usually only two lines of the α -methylene triplet are clearly discernible. The third or low-field line of this triplet often appears as a kind of "shoulder" to the center-band.

- (2) F. E. Luddy, R. A. Barford, and R. W. Riemenschneider, *J. Am. Oil Chem. Soc.*, **37**, 447 (1960).
- (3) F. D. Gunstone and W. C. Russell, *J. Chem. Soc.*, **1955**, p 3782.
- (4) C. Y. Hopkins and H. J. Bernstein, *Can. J. Chem.*, **37**, 775 (1959).
- (5) J. M. Purcell and H. Susi, *Appl. Spectry.*, **19**, 105 (1965).

(1) J. M. Purcell, S. G. Morris, and H. Susi, *ANAL. CHEM.*, **38**, 588 (1966).

Table I. Identification of the Chemical

Compound	Spectrum No.	Proton ^a	Multiplet position ^b
$\begin{array}{ccccccc} a & b & d & & d & b & e & f \\ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 5-Octadecynoic acid	1A	a	0.88
		b	1.26
		c	1.67
		c	1.75
		c	1.87
		d	2.08
		e	2.43
		f	11.82
$\begin{array}{ccccccc} a & b & d & & d & b & e & f \\ \text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_2\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 6-Octadecynoic acid	1B	a	0.88
		b	1.26
		c	1.60
		d	2.12
		e	2.33
		f	11.60
$\begin{array}{ccccccc} a & b & d & & d & b & e & f \\ \text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_3\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 7-Octadecynoic acid	2A	a	0.88
		b	1.27
		c	1.48
		d	2.08
		e	2.31
		f	11.77
$\begin{array}{ccccccc} a & b & d & & d & b & e & f \\ \text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_4\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 8-Octadecynoic acid	2B	a	0.89
		b	1.30
		c	1.43
		d	2.08
		e	2.31
		f	11.82
$\begin{array}{ccccccc} a & b & d & & d & b & e & f \\ \text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_5\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 9-Octadecynoic acid	2C	a	0.89
		b	1.32
		c	1.37
		d	2.07
		e	2.30
		f	11.57
$\begin{array}{ccccccc} a & b & d & & d & b & e & f \\ \text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_3\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \end{array}$ Methyl 7-octadecynoate	3A	a	0.88
		b	1.28
		c	1.45
		d	2.08
		e	2.22
		f	3.58
$\begin{array}{ccccccc} a & b & d & & d & b & e & f \\ \text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_4\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \end{array}$ Methyl 8-octadecynoate	3B	a	0.88
		b	1.29
		c	1.40
		d	2.07
		e	2.21
		f	3.58

The presence of a carbon-carbon triple bond in the methylene chain of a long-chain molecule has a deshielding effect upon methylene groups on either side of the triple bond. Therefore, in addition to the lines appearing in the spectrum of a saturated acid, the spectrum of an acetylenic acid exhibits another, often broad, triplet in the vicinity of $\delta = 2.1$.

Several of the acetylenic acids produce one or more anomalous lines in the region $\delta = 1.2$ to 1.6. The assignment of these lines is not obvious, because the remainder of the observed lines would seem *a priori* to account for all of the protons in the molecule. Nevertheless, observed regularities strongly suggest that the anomalous lines are due to the presence of the carbon-carbon triple bond in the acetylenic acid. Moreover, the number and position of these lines can be used to indicate the position of the triple bond. The spectra will be discussed by considering the spectral effects as the triple bond is moved from the 5-position to the 15-position.

Triple Bond in the 5- through 9-Positions. The introduction of a carbon-carbon triple bond into the 5-position of a C_{18} straight-chain acid has a deshielding effect upon the methyl-

ene groups in the 4- and 7-positions. The resulting broadened triplet occurs at $\delta = 2.08$ —i.e., 0.82 ppm downfield from the chain methylene band (Figure 1A). The terminal methyl triplet and the chain methylene band appear in the usual positions of $\delta = 0.88$ and $\delta = 1.26$, respectively. The chemical shift of the α -methylene group ($\delta = 2.43$) is slightly higher than usual. The acid proton appears as a broad band at $\delta = 11.82$. The terminal methyl triplet is quite broad, whereas the α -methylene triplet is sharper than usual so that the low-field line is clearly separated from the center-band. These lines would seem to account for all the protons of the molecule. However, three anomalous, broad lines appear at $\delta = 1.67, 1.75$, and 1.87, respectively.

On moving the triple bond to the 6-position the spectrum (Figure 1B) changes significantly. The terminal methyl triplet ($\delta = 0.88$) and the chain methylene band ($\delta = 1.26$) are essentially the same in appearance and position. The α -methylene triplet ($\delta = 2.33$) is shifted slightly upfield and is noticeably broader. The acid proton line at $\delta = 11.60$ is sharper even though the solution concentration is approximately the same as that of the 5-isomer. The methylenes

Shifts of Various Protons

Compound	Spectrum No.	Proton ^a	Multiplet position ^b
$\begin{array}{ccccccc} a & b & c & & c & b & d \\ \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{C}\equiv\text{C}-\text{C}\equiv\text{CCH}_2(\text{CH}_2)_6\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 10,12-Octadecadiynoic acid	4A	a b c d	0.92 1.38 2.19 2.33
$\begin{array}{ccccccccccc} a & b & d & h & g & & e & b & f \\ \text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{CH}=\text{CH}-\text{C}\equiv\text{CCH}_2(\text{CH}_2)_6\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ <i>trans</i> -Octadec-11-en-9-ynoic acid	4B	a b c c d e f g h	0.91 1.30 1.35 1.42 2.11 2.26 2.36 5.43 6.00
$\begin{array}{ccccccc} a & b & c & & c & b & d & e \\ \text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_6\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 10-Octadecynoic acid	5A	a b c d e	0.88 1.33 2.06 2.28 11.72
$\begin{array}{ccccccc} a & b & c & & c & b & d & e \\ \text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_7\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 11-Octadecynoic acid	5B	a b c d e	0.88 1.31 2.05 2.27 11.71
$\begin{array}{ccccccc} a & b & c & & c & b & d & e \\ \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_8\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 12-Octadecynoic acid	6A	a b c d e	0.90 1.29 2.06 2.28 11.52
$\begin{array}{ccccccc} a & b & c & & c & d & d & e \\ \text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_9\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 13-Octadecynoic acid	6B	a b c d e	0.91 1.30 2.07 2.30 10.67
$\begin{array}{ccccccc} a & c & & c & b & d & e \\ \text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2(\text{CH}_2)_{11}\text{CH}_2\text{C}(=\text{O})\text{OH} \end{array}$ 15-Octadecynoic acid	6C	a b c d e	0.91 1.30 2.07 2.30 10.67

^a A letter appearing in this column but not in the structural formula indicates the anomalous line(s).

^b δ = values.

adjacent to the triple bond now appear as a broad unresolved band at $\delta = 2.12$. Only one anomalous line appears as a broad band at $\delta = 1.60$.

Placing the triple bond in the 7-position we see that the spectrum is very similar to that of the 6-isomer. The only significant change is that of the anomalous line (see Table I). Figure 2A shows the superposition of the anomalous line on the low-field side of the chain methylene band. This line ($\delta = 1.48$) is 0.12 ppm upfield with respect to the same line in the spectrum of the 6-isomer and has a much smaller line width.

The spectrum of the 8-isomer differs from that of the 7-isomer only in the position of the anomalous line ($\delta = 1.43$). The line shape remains essentially the same. The positions of the multiplets are given in Table I. The spectrum is given in Figure 2B. The change in position of the triple bond has again produced an upfield shift of the anomalous line. However, the shift of the anomalous line in the 8-isomer spectrum relative to the 7-isomer spectrum ($1.43-1.48 = -0.05$ ppm) is smaller than the same shift for the 7-isomer relative to the 6-acid ($1.48-1.60 = -0.12$ ppm).

In the spectrum of the 9-isomer (Figure 2C), the anomalous line is 0.06 ppm upfield ($\delta = 1.37$) with respect to that in the 8-isomer spectrum. Thus the anomalous line(s) change in multiplicity, shape, and position as the triple bond position is incremented from the 5- to the 9-position.

Conjugated Double-Triple Bonds. *trans*-Octadec-11-en-9-ynoic acid (Figure 3B), which contains a double and a triple bond in a conjugated sequence presents an interesting comparison. The presence of the double bond produces three lines (at $\delta = 1.30$, 1.35, and 1.42) in the chain methylene position. The line at $\delta = 1.30$ has been assigned to the chain methylene groups. Thus there are two anomalous lines at $\delta = 1.35$ and 1.42. It cannot be said at this point whether these two lines constitute a doublet or two singlets. Differences are also observed in the region $\delta = 2.0$ to $\delta = 2.5$, because the methylene group adjacent to the double bond is not magnetically equivalent to that adjacent to the triple bond. For this part of the spectrum of *trans*-octadec-11-en-9-ynoic acid one would predict three overlapping multiplets—i.e., a broadened triplet for the methylene group adjacent to the triple bond, a broadened quartet for the methylene group

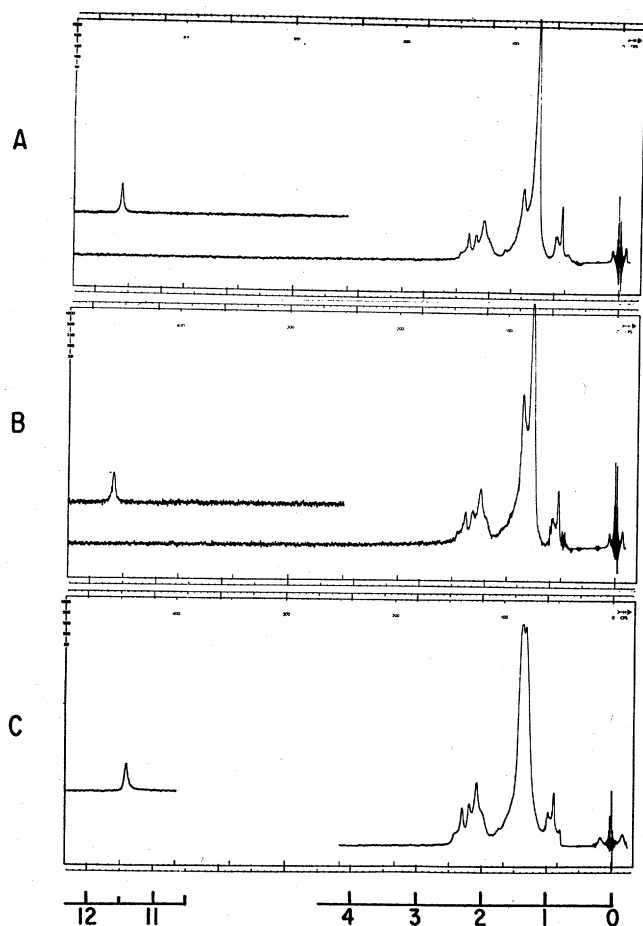


Figure 2. A. 7-Octadecynoic acid. B. 8-Octadecynoic acid. C. 9-Octadecynoic acid

adjacent to the double bond, and an α -methylene triplet. The observed spectrum probably fits this description, although the three multiplets are discernible only with some difficulty. Chemical shift assignments are as follows: the methylene group adjacent to the double bond at $\delta = 2.11$, the methylene

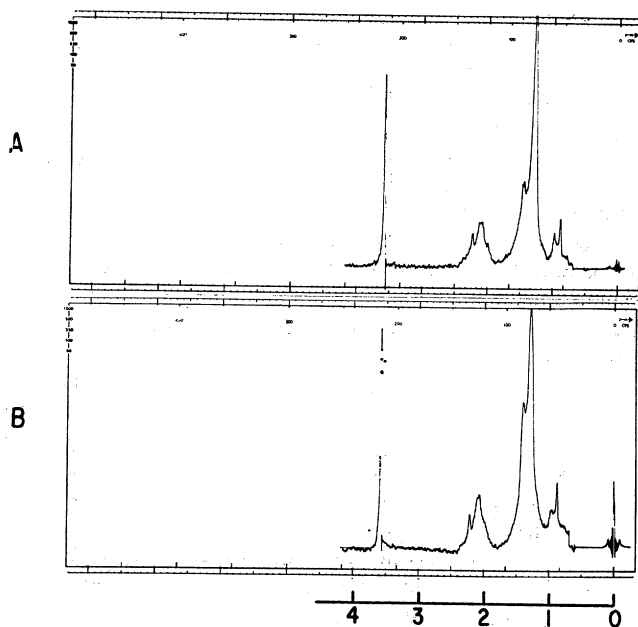


Figure 3. A. 10,12-Octadecadiynoic acid. B. *trans*-Octadec-11-en-9-ynoic acid

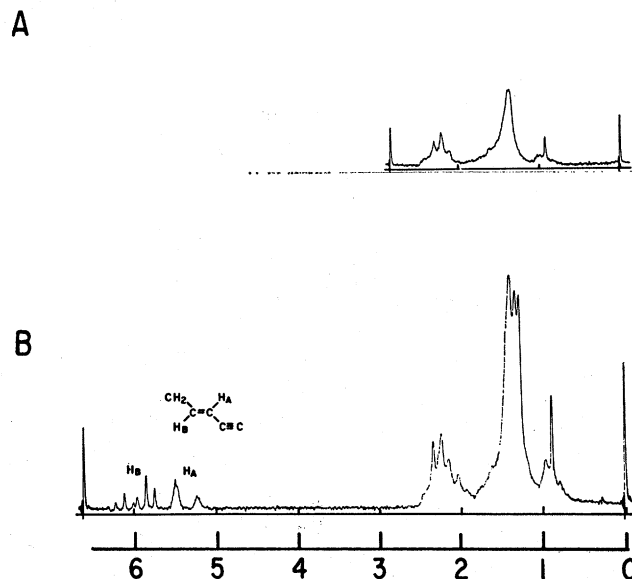


Figure 4. A. Methyl 7-octadecynoate. B. Methyl 8-octadecynoate

group adjacent to the triple bond at $\delta = 2.26$, and the α -methylene group at $\delta = 2.36$.

Methyl Esters. Long-chain molecules exist in a large number of conformations. In some conformations the molecule is folded back upon itself (6). For the acetylenic acids under consideration such folded conformations could permit an interaction between the acid proton and the π electrons of the triple bond. The occurrence of the anomalous lines might be correlated with this phenomenon. However, the spectra of the methyl esters of the 7- and 8-isomers show conclusively that this is not the case. The two spectra are given in Figure 4, A and B. The anomalous line is observed in each spectrum with its position unchanged with respect to the spectrum of the corresponding acid.

(6) C. R. Eddy, *J. Chem. Phys.*, **38**, 1032 (1963).

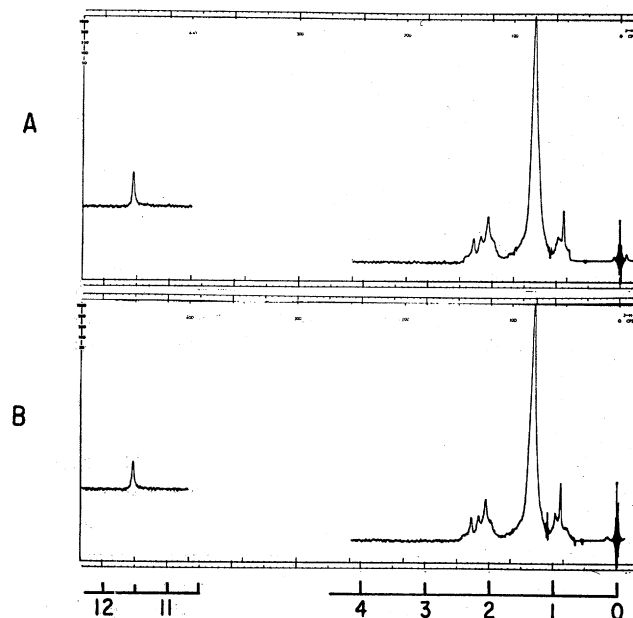


Figure 5. A. 10-Octadecynoic acid. B. 11-Octadecynoic acid

Triple Bond in the 10-, 11-, 12-, 13-, and 15-Position. The introduction of a triple bond into the 10-, 11-, 12-, 13-, or 15-position eliminates the occurrence of anomalous lines. The spectra of the 10- and 11-isomers are given in Figure 5, *A* and *B*. The observed lines are just those which would be predicted from a comparison with the spectra of unsaturated fatty acids containing a double bond in a similar position (*I*). Except for the acid proton resonance the observed line positions in the spectra of the 10- and 15-isomers are nearly identical. The greatest difference between corresponding positions is on the order of 0.02 ppm. The proximity of the triple bond to the terminal methyl end of the chain in the 15-isomer causes the triplets due to the terminal group and due to the methylene groups adjacent to the triple bond to be sharper and more clearly discernible than the corresponding multiplets in the spectra of the 10-, 11-, 12-, and 13-isomers.

10,12-Octadecadiynoic acid yields a similar spectrum (Figure 3*A*) in which no anomalous lines appear. The observed multiplet positions (Table I) are each slightly downfield from those of the other five isomers. The greatest difference between corresponding positions is 0.14 ppm for the methylene groups adjacent to the triple bonds.

ACKNOWLEDGMENT

We are grateful to S. G. Morris for preparing *trans*-octadec-11-en-9-ynoic acid and the two methyl esters, and to R. J. Szamborski for obtaining the spectra.

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